# Microstructure and Properties of Poly(amide urethane)s

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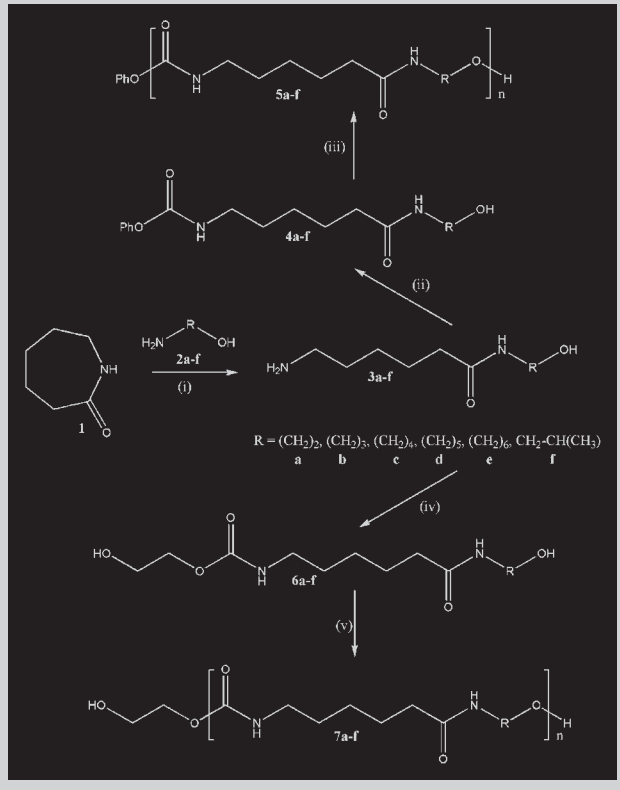
**Summary:** Poly(amide urethane)s were prepared from ε-caprolactam, amino alcohols, and diphenyl carbonate or ethylene carbonate in three steps. Polycondensation was performed either with α-hydroxy-ω-*O*-phenyl urethanes or with α-hydroxy-ω-*O*-hydroxyethyl urethanes; it was found that the reactivity at 90 °C of the first is much higher than that of the latter. For nearly equal reactivity, the temperature for the polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes had to be increased from 90 °C to 150 °C. The microstructure of the resulting poly(amide urethane)s differs by the content of urea groups in the polymer chains, which is 5% for poly(amide urethane)s prepared from α-hydroxy-ω-*O*-phenyl urethanes and 15% for poly(amide urethane)s prepared from α-hydroxy-ω-*O*-hydroxyethyl urethanes. As a consequence, the thermal properties of the poly(amide urethane)s differ slightly.




Synthesis of poly(amide urethane)s.

# Microstructure and Properties of Poly(amide urethane)s: Comparison of the Reactivity of α-Hydroxy-ω-*O*-phenyl Urethanes and α-Hydroxy-ω-*O*-hydroxyethyl Urethanes

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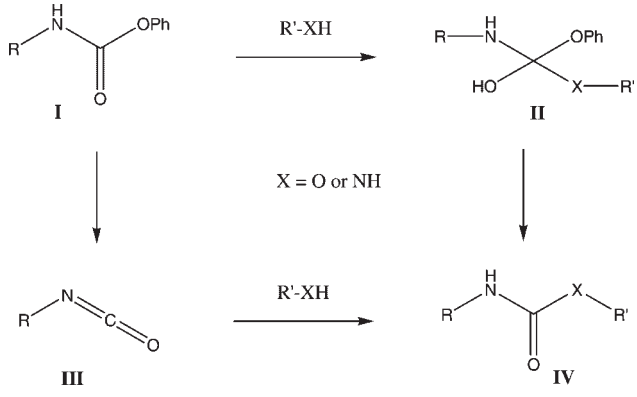
**Keywords:** alternating poly(amide urethane)s; oligomers with specific end groups; polycondensation; structure-property relations

## Introduction

Commercially manufactured polyurethanes are prepared from diisocyanates, diols, (and diamines) and have found broad applications.[1] The microstructure of these technical polyurethanes contains besides urethane also urea groups in variable concentration. Polyurethanes with a uniform microstructure were obtained by ring-opening polymerization

of cyclic urethanes[2–6] and by polycondensation of α-hydroxy-ω-*O*-phenyl urethanes.[7] α-Hydroxy-ω-*O*-phenyl urethanes can be considered either as blocked isocyanates or as activated urethanes. At lower temperatures (≈100 °C) in the presence of catalysts, *O*-phenyl urethanes **I** react with nucleophiles in the sense of an activated urethane by substitution of the phenoxy group – reaction sequence **I** → **II** → **IV** while at higher temperatures (≈170 °C) the "deblocking" reaction with elimination of phenol and formation of an isocyanate intermediate is more probable – reaction sequence **I** → **III**. In the presence of a nucleophile, the end product of this reaction is a urethane or a urea **IV**, as can be seen in the following reaction scheme:




Besides phenol, a large number of blocking agents for isocyanates has been studied, e.g., oximes, alcohols, and ε-caprolactam.[8–10] In recent times, special attention has been given to *N,N′*-carbonylbis(ε-caprolactam), a solid, non-toxic carbonic acid derivative from the family of blocked isocyanates which has become a versatile reagent for coupling reactions and for the preparation of thermosets and reactive resins.[11]

The present paper reports on the synthesis of alternating poly(amide urethane)s using ε-caprolactam, amino alcohols, and diphenyl carbonate or ethylene carbonate as starting materials with special emphasis on the microstructure and the thermal properties of the resulting poly(amide urethane)s. Both carbonic acid derivatives are obtained without use of phosgene: ethylene carbonate is prepared from ethylene oxide and carbon dioxide,[12] and diphenyl carbonate from phenol and urea,[12] or phenol and carbon monoxide.[13] In addition, this paper evaluates the reactivity of α-hydroxy-ω-*O*-phenyl urethanes relative to α-hydroxy-ω-*O*-hydroxyethyl urethanes in polycondensation reactions.

## Experimental Part

*Materials*

ε-Caprolactam (BASF), 2-amino-1-ethanol (Aldrich), 3-amino-1-propanol (Aldrich), 1-amino-2-propanol (Aldrich), 4-amino-1-butanol (Acros), 5-amino-1-pentanol (Fluka), 6-amino-1-hexanol (Fluka), diphenyl carbonate (Fluka), ethylene carbonate (Acros), dimethyl carbonate (Aldrich), dibutyltin dimethoxide (Aldrich), formic acid, and diethyl ether were used as received. Methylene chloride and ethanol were distilled before use.

Polycondensation reactions were carried out in an inert gas atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

*Measurements*

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Deuterated chloroform ($CDCl_3$), trifluoroacetic acid (TFA-*d*), and dimethyl sulfoxide (DMSO-$d_6$) were used as solvents, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high-pressure liquid chromatography pump (Bischoff HPLC pump 2200) and a refractive index detector (Waters 410). The eluting solvent was *N,N*-dimethylacetamide (DMAC) with 2.44 g · l$^{-1}$ LiCl with a flow rate of 0.8 ml · min$^{-1}$. Four columns with MZ-DVB gel were applied; length of each column 300 mm, diameter 8 mm, diameter of gel particles 5 μm, nominal pore widths 100, 100, $10^3$, and $10^4$ Å. Calibration with polystyrene standards was used for the estimation of molecular weights and polydispersities.

Thermogravimetric analyses (TGA) were performed on a TG 209 with a TA-System-Controller TASC 414/2 from Netzsch. The measurements were performed in nitrogen atmosphere with a heating rate of 10 K · min$^{-1}$.

Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204 in nitrogen atmosphere with a heating rate of 10 K · min$^{-1}$.

*Preparation of Poly(amide urethane)s **5a-f***

The synthesis of poly(amide urethane)s using ε-caprolactam and amino alcohols with diphenyl carbonate was reported in a previous paper, and $^1$H and $^{13}$C NMR spectra in DMSO-$d_6$ and TFA-*d* were in accord with the proposed structures.[14]

*Preparation of α-Hydroxy-ω-O-hydroxyethyl Urethanes **6b***

Method A: α-Hydroxy-ω-amine **3b** (10.05 g, 53.48 mmol) and ethylene carbonate (5.66 g, 64.3 mmol) were dissolved in water (6 ml), and the solution was stirred at room temperature for 65 h. Volatiles were removed in vacuum at 70–80 °C.

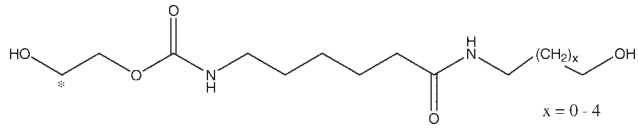
This procedure was used for the preparation of α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a**, **c**, **d**, **e**.

Method B: α-Hydroxy-ω-amine **3f** (20.82 g, 110.76 mmol) and ethylene carbonate (48.79 g, 554.41 mmol) were stirred at 60 °C for 24 h. Volatiles were removed in vacuum at 70–80 °C.

Reaction conditions, yields, and characteristic NMR resonance lines of the α-hydroxy-ω-*O*-hydroxyethyl urethanes are summarized in Table 1.

Table 1. Synthesis and characteristics of α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a-f**.




| No. | Time | Yield | Characteristic $^1$H and $^{13}$C chemical shift in DMSO-$d_6$ $\delta$ | | | | |
|---|---|---|---|---|---|---|---|
| | h | % | ppm | | | | |
| | | | HO–**CH$_2^*$**– | **–CH$_2$**–O– | –O–CO–NH–**CH$_2$**– | –CO–NH–**CH$_2$**– | **–CH$_2$**OH |
| **6a** | 57 | 87 | 3.52 | 3.94 | 2.95 | 3.10 | 3.38 |
| | | | 59.91 | 65.36 | 40.06 | 41.37 | 59.44 |
| **6b** | 65 | 85 | 3.53 | 3.94 | 2.95 | 3.09 | 3.39 |
| | | | 59.84 | 65.75 | 40.46 | 35.95 | 58.76 |
| **6c** | 48 | 88 | 3.52 | 3.93 | 2.95 | 3.01 | 3.38 |
| | | | 60.40 | 65.36 | 40.07 | 38.26 | 59.44 |
| **6d** | 57 | 86 | 3.52 | 3.93 | 2.94 | 3.01 | 3.37 |
| | | | 60.60 | 65.36 | 40.07 | 38.38 | 59.44 |
| **6e** | 44 | 91 | 3.52 | 3.93 | 2.94 | 2.99 | 3.37 |
| | | | 60.62 | 65.36 | 40.13 | 38.32 | 59.44 |
| **6f** | 24 | 95 | 3.52 | 3.93 | 2.93 | 2.97 | 3.62[a] |
| | | | 59.45 | 65.36 | 40.22 | 46.28 | 65.24[a] |

[a] –**CH**(CH$_3$)–OH

*Preparation of Poly(amide urethane)s **7a-f***

α-Hydroxy-ω-*O*-hydroxyethyl urethane **6b** (2.00 g, 7.25 mmol) was heated with $Bu_2Sn(OCH_3)_2$ (5 wt.-%) to 150 °C in inert gas atmosphere. The polycondensation was performed for 1 h at normal pressure and for 5 h at reduced pressure ($10^{-2}$ mbar), and the condensate was removed from the reaction vessel by distillation. The crude product was dissolved in HCOOH, precipitated into diethyl ether, filtered, and dried at 50 °C under reduced pressure.

The procedure described for the preparation of **7b** was used for all poly(amide urethane)s **7a-f** (Table 2).

Table 2. Poly(amide urethane)s **7a-f** obtained via polycondensation of **6a-f** in bulk at 150 °C.

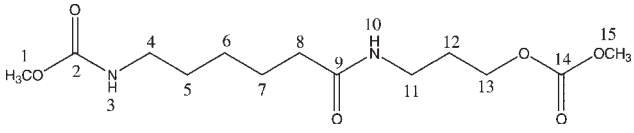
| No. | Time | $\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$[c] | Yield | Characteristic $^1$H and $^{13}$C chemical shift in DMSO-$d_6$ $\delta$ | | | |
|---|---|---|---|---|---|---|---|---|
| | h | | | % | ppm | | | |
| | | | | | –CH$_2$–NH–**CO**– | –CO–NH–**CH$_2$**– | –NH–**CH$_2$**– | **–CH$_2$**–O– |
| **7a** | 1[a] + 3[b] | 7 100 | 1.51 | 85 | – | 2.95 | 3.23 | 3.92 |
| | | | | | 156.04 | 37.47 | 38.11 | 62.10 |
| **7b** | 1[a] + 5[b] | 10 900 | 1.60 | 85 | – | 2.92 | 3.06 | 3.91 |
| | | | | | 156.60 | 40.41 | 35.73 | 61.89 |
| **7c** | 1[a] + 3[b] | 7 600 | 1.74 | 97 | – | 2.93 | 3.02 | 3.90 |
| | | | | | 156.77 | 40.77 | 38.71 | 63.90 |
| **7d** | 1[a] + 3[b] | 9 500 | 1.52 | 84 | – | 2.94 | 3.00 | 3.89 |
| | | | | | 156.27 | 40.09 | 38.23 | 63.40 |
| **7e** | 1[a] + 3[b] | 7 500 | 1.78 | 85 | – | 2.93 | 3.00 | 3.90 |
| | | | | | 156.28 | 40.07 | 38.23 | 63.41 |
| **7f** | 2[a] + 6[b] | 8 100 | 1.57 | 83 | – | 2.94 | 3.13 | 4.66[d] |
| | | | | | 155.72 | 40.03 | 43.10 | 68.54[d] |

[a] At normal pressure (1 bar).
[b] At reduced pressure ($10^{-2}$ mbar).
[c] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by GPC in DMAC using polystyrene standards.
[d] –**CH**(CH$_3$)–OH.

*Preparation of α-O-Methyl carbonate-ω-O-methyl Urethane*

α-Hydroxy-ω-amine **3b** (1.17 g, 6.2 mmol) and dimethyl carbonate (7.01 g, 77.8 mmol) were refluxed at 95 °C for 15 h. For purification, the resulting solution was precipitated into diethyl ether, filtrated, and dried at 50 °C under reduced pressure.



$^1$H NMR (DMSO-$d_6$): $\delta = 1.21$ (m, 2H, H-6), 1.34–1.48 (m, 4H, H-5, H-7), 1.70 (m, 2H, H-12), 2.03 (t, 2H, H-8), 2.94 (dt, 2H, H-4), 3.08 (dt, 2H, H-11), 3.49 (s, 3H, H-1), 3.68 (s, 3H, H-15), 4.06 (t, 2H, H-13), 7.11 (t, 1H, H-3), 7.94 (t, 1H, H-10).

$^{13}$C NMR (DMSO-$d_6$): $\delta = 25.34$ (C-7), 26.24 (C-6), 28.74 (C-5), 29.56 (C-12), 35.32 (C-8), 35.65 (C-11), 40.45 (C-4), 51.42 (C-1), 54.84 (C-15), 65.78 (C-13), 155.49 (C-14), 157.00 (C-2), 172.46 (C-9).

## Results and Discussion

The use of carbon dioxide for the preparation of polymers is an excellent option from an economical and particularly, from an ecological point of view. Ethylene carbonate and diphenyl carbonate are two examples of reagents (monomers) used in polymer synthesis which are prepared from ethylene oxide and carbon dioxide,[12] from phenol and urea[12] or from phenol and carbon monoxide.[13] In this paper we describe the use of diphenyl carbonate and ethylene carbonate for the preparation of alternating poly(amide urethane)s with special emphasis on the differences in the microstructure and thermal properties of the resulting polymers.

Alternating poly(amide urethane)s **5a-f** and **7a-f** were obtained from ε-caprolactam (**1**), a homologous series of amino alcohols **2a-e** and 1-amino-2-propanol **2f** with diphenyl carbonate or ethylene carbonate (Scheme 1). The synthesis of poly(amide urethane)s **5a-f** using diphenyl carbonate as carbonic acid source has been described in a previous paper.[14] Due to the toxicity of phenol, the use of ethylene carbonate as carbonic acid source seems to be an excellent alternative for diphenyl carbonate leading to poly(amide urethane)s with nearly the same microstructure but different end groups as will be shown in this paper.

The synthesis of α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a-f** was performed employing α-hydroxy-ω-amines **3a-f** and ethylene carbonate in water as reaction medium at room temperature. The crude products were obtained in high purity as was deduced from NMR analysis. The resonance lines of the methylene groups adjacent to the newly formed urethane group and the resonance lines of the urethane confirm that under the reaction conditions only the amine group and not the hydroxy group has reacted ($^1$H NMR and $^{13}$C NMR data (in DMSO-$d_6$) for **3b** are: $\delta = 2.48$ and 41.90 for $\mathbf{CH_2}NH_2$, and $\delta = 3.38$ and 58.70 for $\mathbf{CH_2}OH$; for **6b**: $\delta = 2.95$ and 40.46 for $\mathbf{CH_2}$–NH–CO–O–$CH_2CH_2OH$, $\delta = 3.39$ and 58.76 for $\mathbf{CH_2}OH$, and $\delta = 7.10$ for **NH**–CO–O–).

The polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a-f** was performed with $Bu_2Sn(OCH_3)_2$ as the catalyst at 110, 130, and 150 °C for 1–2 h at normal pressure and 3–6 h at reduced pressure. At 110 °C and 130 °C the conversion was very low. At 150 °C the $\overline{M}_n$ values of polymers **7a-f** were similar as those of polymers **5a-f** obtained upon polycondensation of **4a-f**.

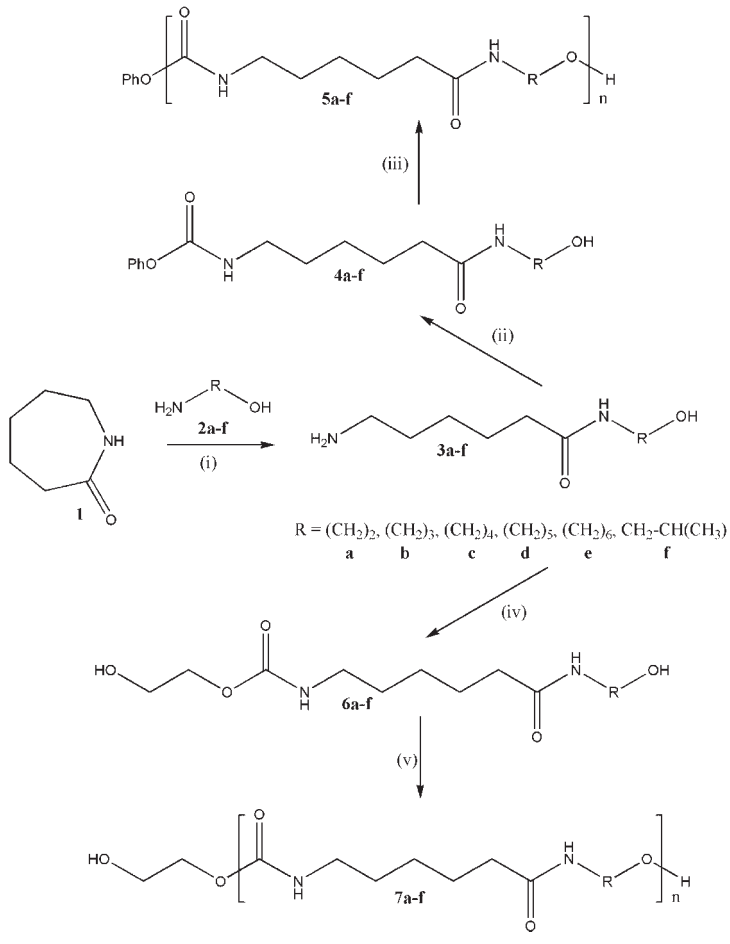
The purified polymers **7a-f** show similarities but also differences to **5a-f**. A comparison of the $^1$H NMR spectra of polymer **5c** and **7c** reveal differences in the microstructure: the ratio of amide, urethane, and urea units is 100/80/5 in polymer **5c** and 100/64/15 in polymer **7c** (Figure 1). The reason for the increase of urea linkages in polymer **7a-f** is the elimination of ethylene carbonate from the chain end at higher temperature and the formation of α-hydroxy-ω-amines. These react subsequently with the α-hydroxy-ω-*O*-hydroxyethyl urethane to produce a urea linkage (Scheme 2). Support for this mechanism of urea linkage formation comes from $^1$H NMR analysis of the condensate, which beside ethylene glycol proves the presence of ethylene carbonate.

At this point, it should be mentioned that all GPC curves of polymers **5a-f** and **7a-f** show unimodal molecular weight distributions, and all NMR spectra show resonance lines, which are in agreement with the proposed structure of alternating poly(amide urethane)s containing variable amounts of urea groups.

Economically and ecologically, there are some advantages of using ethylene carbonate instead of diphenyl carbonate for the preparation of poly(amide urethane)s: (i) Ethylene carbonate has a lower prize. (ii) With ethylene carbonate, aminolysis is performed in water while the aminolysis of diphenyl carbonate requires methylene chloride. (iii) During polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes, ethylene glycol is formed as a by-product, which is less toxic.

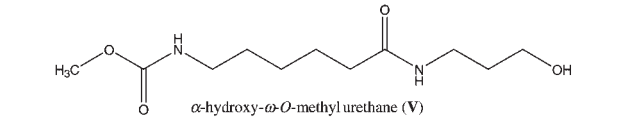
An attempt was also made to prepare poly(amide urethane)s using dimethyl carbonate instead of diphenyl carbonate; the advantage again results from the condensate produced, i.e., methanol instead of phenol. Dimethyl carbonate was reacted with α-hydroxy-ω-amine **3b** to prepare α-hydroxy-ω-*O*-methyl urethanes **V**. The reaction was performed in different solvents, e.g., $CH_2Cl_2$, ethanol, and dimethyl carbonate at different temperatures, e.g., r.t., 60, 70, and 90–95 °C. The following observations based on NMR analyses were made: (i) At room temperature as well as 60 °C in methylene chloride, no conversion was observed. (ii) At room temperature as well as 90 °C in ethanol, no conversion was observed. (iii) By using

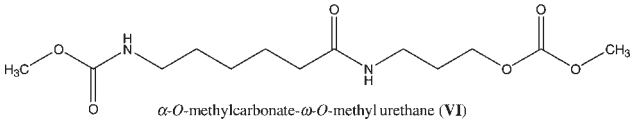
 




Scheme 1. Synthesis of poly(amide urethane)s from ε-caprolactam, amino alcohols, and diphenyl carbonate or ethylene carbonate. (i) **1/2a-f** = 1/5, $H_2O$, $T = 200\,^{\circ}C$ in autoclave, $t = 23-30$ h; (ii) diphenyl carbonate/**3a-f** = 1/1 − 1.5/1, $CH_2Cl_2$, r.t., $t = 24-70$ h; (iii) **4a-f**, 5 wt.-% $Bu_2Sn(OCH_3)_2$, $T = 90\,^{\circ}C$, $t = 1$ h at normal pressure and $t = 3-6$ h at reduced pressure ($10^{-2}$ mbar); (iv) **3a-e**/ethylene carbonate = 1/1.25, $H_2O$, r.t., $t = 44-69$ h; **3f**/ethylene carbonate = 1/5, $T = 60\,^{\circ}C$, $t = 24$ h; (v) **6a-f**, 5 wt.-% $Bu_2Sn(OCH_3)_2$, $T = 150\,^{\circ}C$, $t = 1-2$ h at normal pressure and $t = 3-6$ h at reduced pressure ($10^{-2}$ mbar).

dimethyl carbonate as a solvent and reagent at 95 °C, it was found that both the hydroxy and the amino group reacted leading to the formation of α-methylcarbonate-ω-*O*-methyl urethanes **VI**. (iv) At 60 °C as well as 70 °C with in excess of dimethyl carbonate, a mixture of compounds **V** and **VI** was obtained. As a consequence, dimethyl carbonate is not an alternative reagent for the preparation of poly(amide urethane)s.


α-hydroxy-ω-*O*-methyl urethane (**V**)


α-*O*-methylcarbonate-ω-*O*-methyl urethane (**VI**)

### *Comparision of the Reactivity of α-Hydroxy-ω-O-phenyl Urethanes and α-Hydroxy-ω-O-hydroxyethyl Urethanes*

Preliminary experiments have shown that α-hydroxy-ω-*O*-phenyl urethanes **4a-f** are more reactive than α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a-f**. In order to obtain comparable rates, polycondensation of α-hydroxy-ω-*O*-phenyl urethane **4f** was performed at 90 °C and that of α-hydroxy-ω-*O*-hydroxyethyl urethane **6f** at 150 °C with time dependent analyses of the conversion and of the molecular weight. The conversion and molecular weight were determined by means of $^1H$ NMR spectroscopy by determination of the ratio of end groups (–$CH_2OH$: $\delta =$ 4.15 ppm) and repeating units (–$CH_2O$–: $\delta = 3.95$ ppm). It should be mentioned that the repeating units containing urea groups were neglected. In addition, $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$

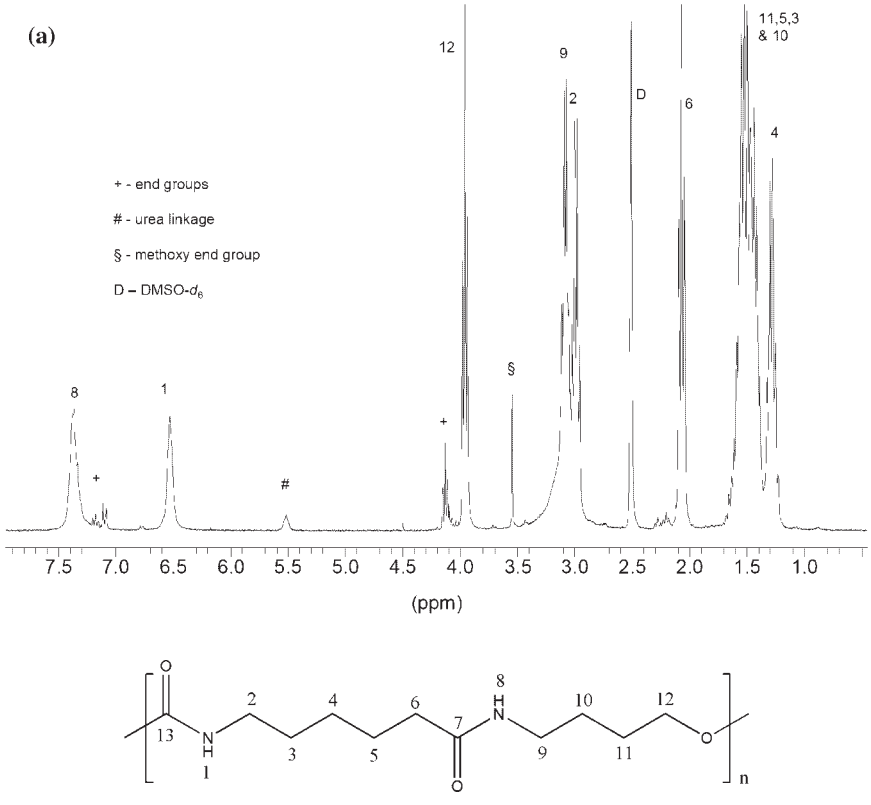
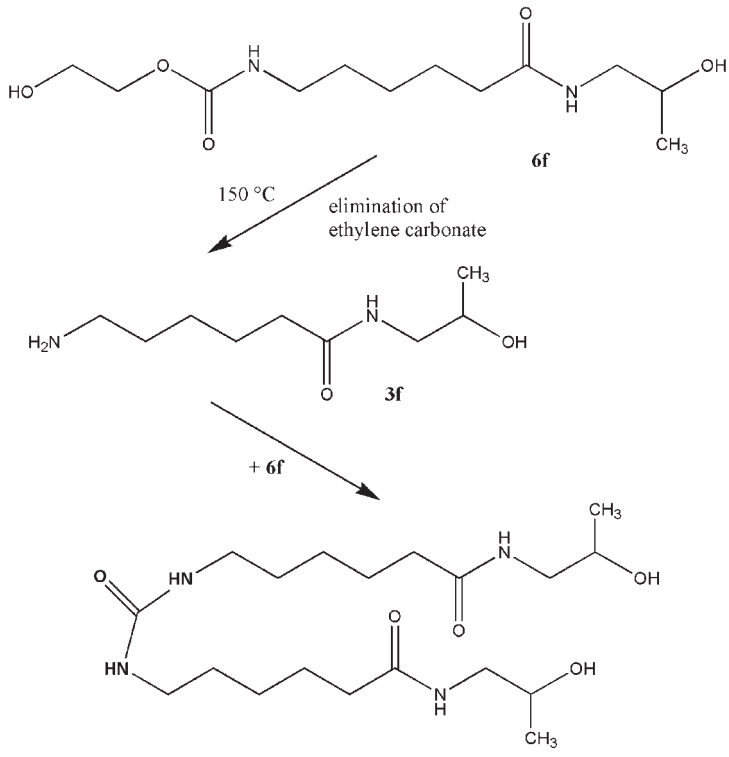



Figure 1. $^1$H NMR spectra of (a) poly(amide urethane) **5c** obtained via polycondensation of α-hydroxy-ω-*O*-phenyl urethane **4c** at 90 °C and (b) poly(amide urethane) **7c** obtained via polycondensation α-hydroxy-ω-*O*-hydroxyethyl urethane **6c** at 150 °C.

were determined by means of GPC using a calibration with polystyrene standards. Typical time dependent GPC elution curves (Figure 2) reveal qualitative data on the reaction rates, e.g., a molecular weight of $\overline{M}_n = 3\,900$ is obtained after 140 min starting with α-hydroxy-ω-*O*-hydroxyethyl urethane **6f** at 150 °C and a molecular weight of $\overline{M}_n = 4\,200$ is obtained after 10 min starting with α-hydroxy-ω-*O*-phenyl urethane **4f** at 90 °C. It should be noted that all GPC curves are unimodal showing some resolution of the oligomers.

The dependence of $\overline{M}_n$ on time was determined for the polycondensation of **4f** and **6f**. Figure 3a shows that even at 150 °C the conversion of end groups is lower for hydroxy-




Scheme 2. Formation of poly(amide urethane)s with urea linkages.

ethyloxy activated urethanes than for phenoxy activated urethane groups. In other words, the nucleophilic substitution of phenol is a faster reaction than the substitution of ethylene glycol due to the fact that phenol is the better leaving group. Under these conditions the average degree of polymerization is approximately 5. The results obtained by GPC are very similar, again a saturation curve is observed; however, by using a polystyrene calibration the molecular weights obtained are by a factor of 6 higher. The molecular weight distribution shows values of 1.6.

The dependence of $\overline{M}_n$ on conversion (Figure 4a) shows a characteristic shape. At conversions below 50% (where the molecular weight of the end groups has a high contribution), the $\overline{M}_n$ values of the polymers derived from α-hydroxy-ω-*O*-phenyl urethanes **4f** are higher than the $\overline{M}_n$ values of the polymers derived from α-hydroxy-ω-*O*-hydroxyethyl urethanes **6f**. At a conversion of 75%, the two curves are nearly identical as would be expected. The dependence of $\overline{M}_n$ on conversion for the two monomers clearly shows that α-hydroxy-ω-*O*-phenyl urethane **4f** has a higher reactivity

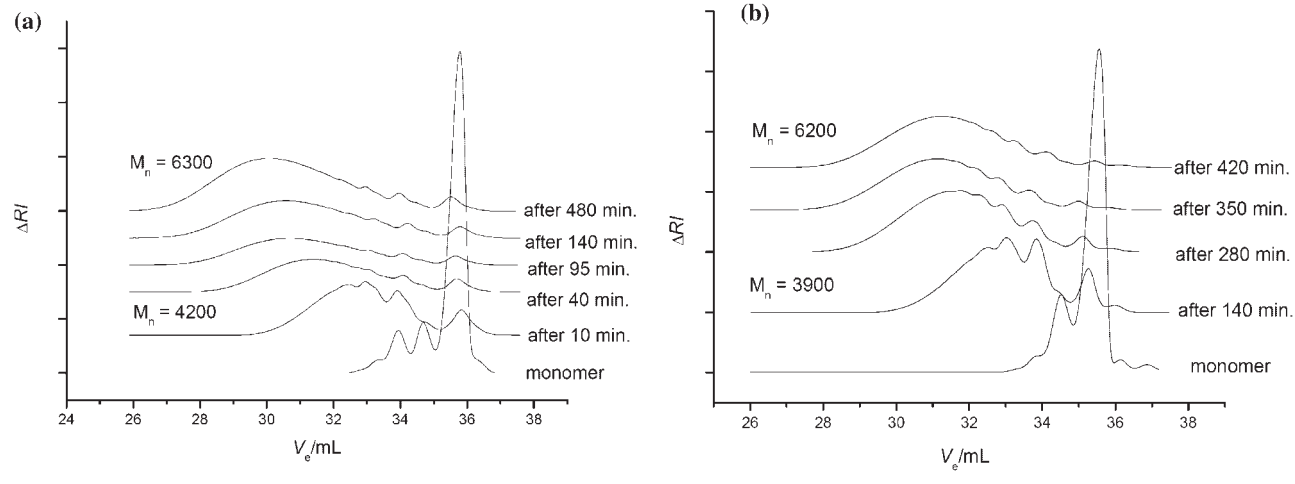



Figure 2. GPC trace of poly(amide urethane)s at various reaction times (a) polycondensation of **4f** at 90 °C in bulk (b) polycondensation of **6f** at 150 °C in bulk.

than α-hydroxy-ω-*O*-hydroxyethyl urethane **6f**; for similar conversions the temperature must be raised from 90 °C to 150 °C.

### *Thermal Properties*

In order to determine the influence of the microstructure and the end groups on the thermal properties, poly(amide urethane)s **5a-e** and **7a-e** were analyzed by means of TGA and DSC.

The TGA thermograms of poly(amide urethane)s **5a-e** and **7a-e** (Figure 5) show a dependence of the degradation temperature on microstructure and possibly on end groups.

There are several similarities between the degradation of the poly(amide urethane)s **5a-e** and **7a-e**: (i) The degradation temperature increases with increasing number of methylene groups in both series of poly(amide urethane)s. (ii) For 2-amino-1-ethanol, 3-amino-1-propanol, and 4-amino-1-butanol in the repeating units, a clear two step decomposition is observed, while this is not observed for 5-amino-1-pentanol and 6-amino-1-hexanol. This indicates that the polymers decompose on different mechanisms: those with lower amino alcohols in the repeating unit decompose by back-biting reactions with formation of cyclic urethanes while those with a higher number of methylene groups in the repeating unit show random chain cleavage with formation of isocyanates which is characteristic for urethane linkages. This assumption is supported by investigations on the thermal decomposition of poly(amide urea)s where we have isolated the corresponding five- and six-membered cyclic ureas.[15]

A comparison of a 5, 10, 50, and 90% weight loss of the polymers as a function of temperature shows no significant difference between the two series of polymers. According to Table 3, the temperature at which 50% weight loss occurs increases with increasing number of methylene groups in both series of poly(amide urethane)s **5a-e** and **7a-e**.

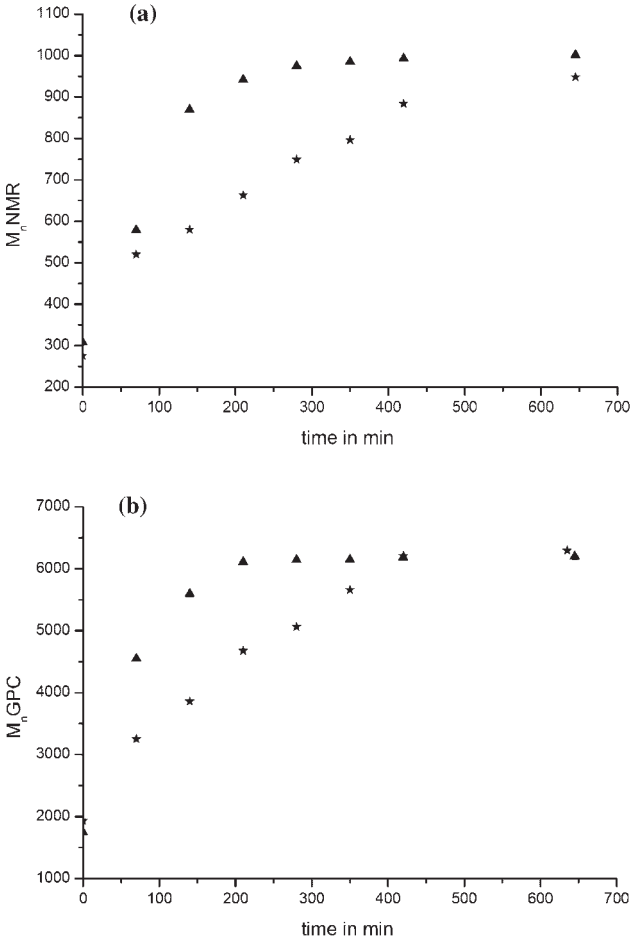



Figure 3. $\bar{M}_n$ as a function of time; (a) $\bar{M}_n$ determined by $^1$H NMR (b) $\bar{M}_n$ determined by GPC. (▲) polycondensation of **4f** in bulk at 90 °C; (*) polycondensation of **6f** in bulk at 150 °C.

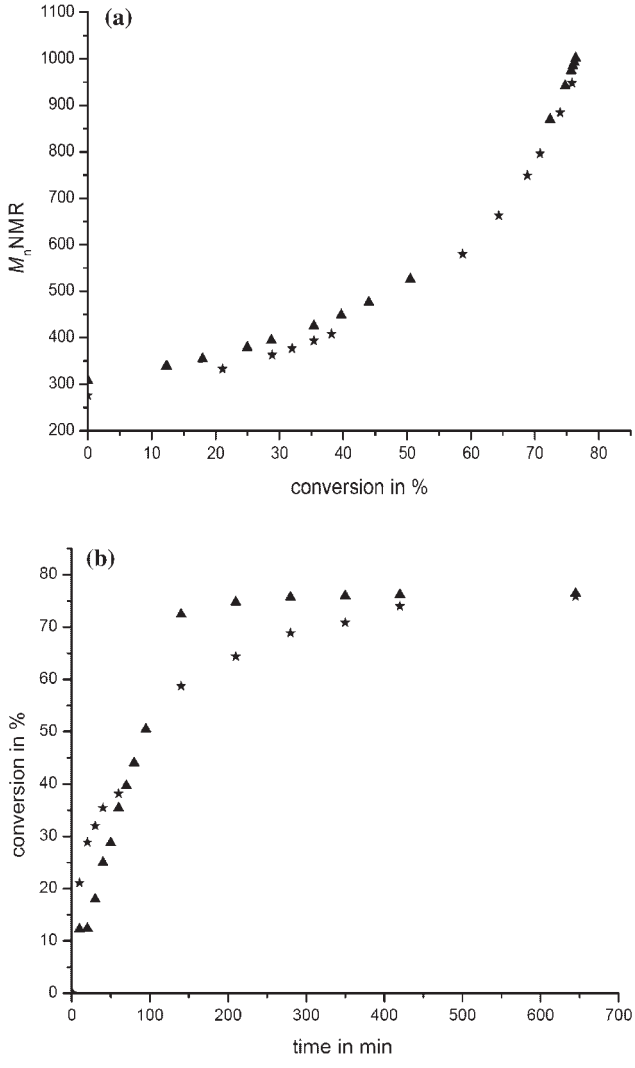



Figure 4. (a) $\bar{M}_n$ as a function of conversion and (b) conversion as a function of time. (▲) polycondensation of **4f** in bulk at 90 °C; (*) polycondensation of **6f** in bulk at 150 °C.

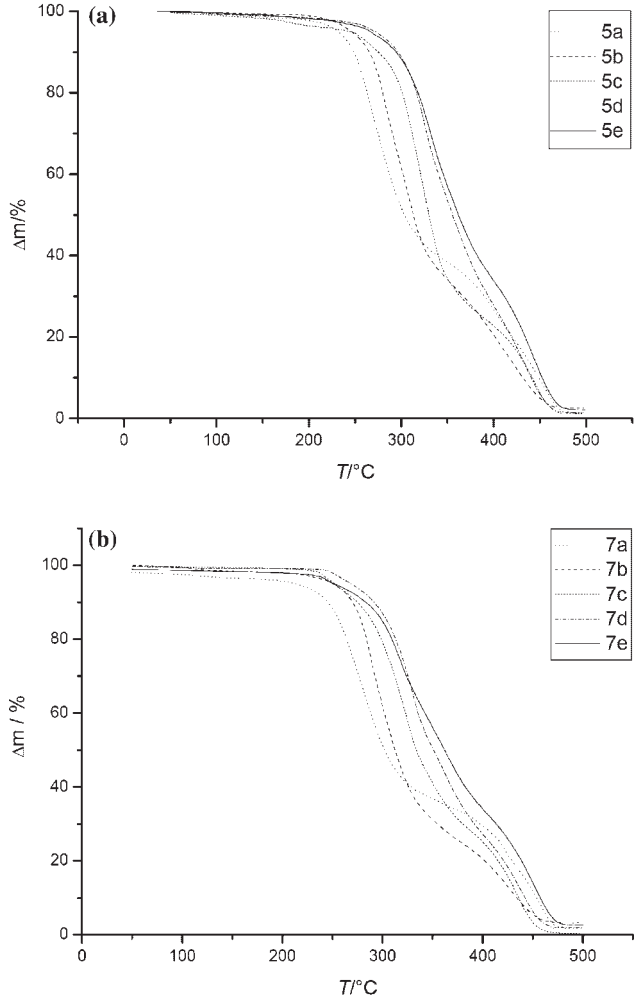



Figure 5. TGA of poly(amide urethane)s: (a) poly(amide urethane) **5a-e** obtained via polycondensation of α-hydroxy-ω-*O*-phenyl urethane **4a-e** at 120 °C; (b) poly(amide urethane)s **7a-e** obtained via polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes **6a-e** at 150 °C.

The DSC measurements show that both series of polymers **5a-e** and **7a-e** are semicrystalline materials. Typical DSC traces reveal on first heating a small crystallization peak before melting (Figure 6). Table 4 summarizes the DSC data obtained for the poly(amide urethane)s **5a-e** and **7a-e**; the differences in melting temperature and enthalpy between the two series of polymers are small; both the melting temperature and the enthalpy are lower for **7a-e**. On cooling, a broad crystallization peak is observed indicating that crystallites of different size are formed, which influences the melting temperature and melting enthalpy on the second heating.

A comparison of the melting points and the melting enthalpies of the first and second heating reveals in most cases slightly lower melting points and definite lower melting enthalpies in the second heating. The conclusion of this experimental result is that from the melt crystallization occurs slowly and annealing would be necessary to increase the degree of crystallinity.

The melting temperature of both series shows that the poly(amide urethane)s with an even number of carbon atoms in the amino alcohol units have a higher melting point than those with an odd number of carbon atoms. This pronounced even-odd effect (Figure 7) was observed before for [*n*]-polyamides,[16] [*n*]-polyurethanes,[7,17] and poly(ester amide)s.[18] A comparison between the two graphs (Figure 7) shows that for poly(amide urethane)s **5a-e** the even-odd effect is more pronounced than for **7a-e**.

## Conclusion

Poly(amide urethane)s from ε-caprolactam, amino alcohols, and ethylene carbonate were prepared in three steps, the last step being the polycondensation of α-hydroxy-ω-*O*-hydroxyethyl urethanes which was performed at 150 °C. These polymers have beside alternating amide and urethane groups, 15% of urea groups which is higher by 10% compared with the poly(amide urethane)s prepared from α-hydroxy-ω-*O*-phenyl urethanes at 90 °C. Due to the higher content of urea groups, the melting points of these poly(amide urethane)s are lower. These oligomeric poly(amide urethane)s with two hydroxy end groups will be

Table 3. Temperature of poly(amide urethane)s **5a-e** and **7a-e** at different weight loss measured by TGA.

| Polymer | $\bar{M}_n$ (GPC) | *T* at 5% weight loss | *T* at 10% weight loss | *T* at 50% weight loss | *T* at 90% weight loss |
|---|---|---|---|---|---|
| | | °C | °C | °C | °C |
| **5a** | 8 900 | 232 | 249 | 303 | 449 |
| **5b** | 7 400 | 245 | 265 | 313 | 432 |
| **5c** | 8 300 | 245 | 275 | 329 | 442 |
| **5d** | 11 500 | 271 | 295 | 356 | 441 |
| **5e** | 7 100 | 266 | 294 | 362 | 453 |
| **7a** | 7 100 | 214 | 246 | 302 | 454 |
| **7b** | 10 900 | 251 | 270 | 313 | 434 |
| **7c** | 7 600 | 252 | 275 | 334 | 436 |
| **7d** | 9 500 | 267 | 292 | 351 | 442 |
| **7e** | 7 500 | 252 | 284 | 362 | 457 |

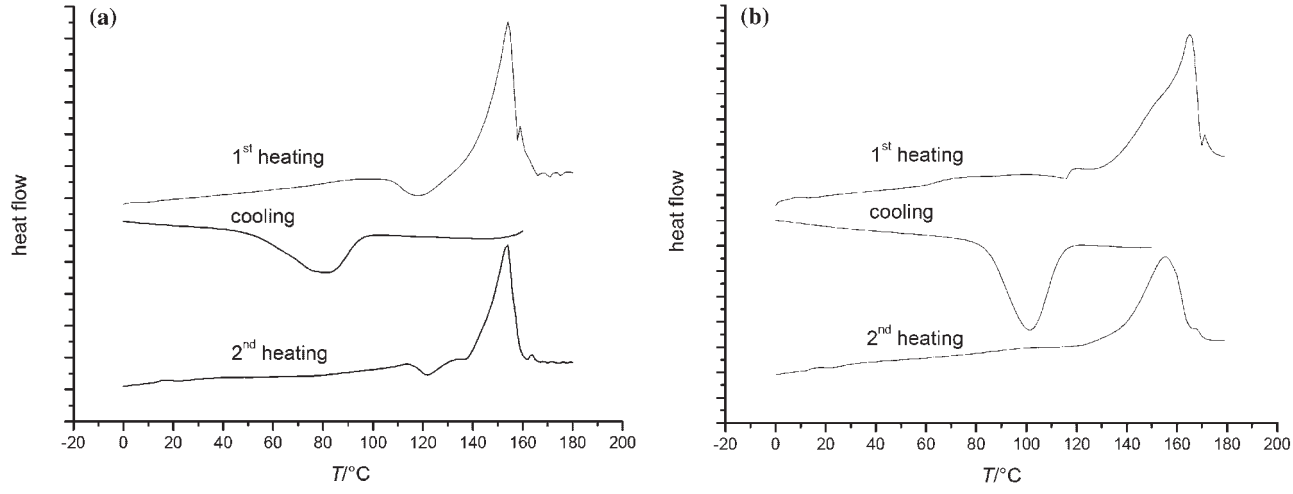



Figure 6. DSC traces of polymers (heating and cooling rate: 10 K · min$^{-1}$). (a) poly(amide urethane) **5b** (b) poly(amide urethane) **7b**.

Table 4. Thermal data of the poly(amide urethane)s **5a-e** and **7a-e** measured by means of DSC (heating and cooling rate 10 K · min$^{-1}$).

| Polymers | $\bar{M}_n$ GPC | First Heating | | Cooling | | Second Heating | |
|---|---|---|---|---|---|---|---|
| | | $T_m$ | $\Delta H_m$ | $T_c$ | $\Delta H_c$ | $T_m$ | $\Delta H_m$ |
| | | °C | J · g$^{-1}$ | °C | J · g$^{-1}$ | °C | J · g$^{-1}$ |
| **5a** | 8 900 | 173.6 | 54.39 | 126.4 | −42.78 | 172.2 | 31.88 |
| **5b** | 7 400 | 154.1 | 80.29 | 81.4 | −35.88 | 153.7 | 41.82 |
| **5c** | 8 300 | 199.9 | 54.42 | 154.0 | −58.85 | 189.4 | 58.47 |
| **5d** | 11 500 | 162.5 | 77.21 | 121.4 | −68.11 | 160.7 | 64.70 |
| **5e** | 7 100 | 171.6 | 66.07 | 125.4 | −59.16 | 169.4 | 53.74 |
| **7a** | 7 100 | 163.1 | 68.24 | 95.4 | −10.57 | 161.4 | 36.06 |
| **7b** | 10 900 | 164.9 | 52.74 | 101.2 | −36.68 | 155.4 | 38.35 |
| **7c** | 7 600 | 180.3 | 59.88 | 139.5 | −52.22 | 175.5 | 52.20 |
| **7d** | 9 500 | 139.4 | 69.74 | 66.7 | −40.09 | 138.9 | 41.77 |
| **7e** | 7 500 | 140.6 | 40.78 | 81.6 | −42.27 | 139.4 | 41.36 |

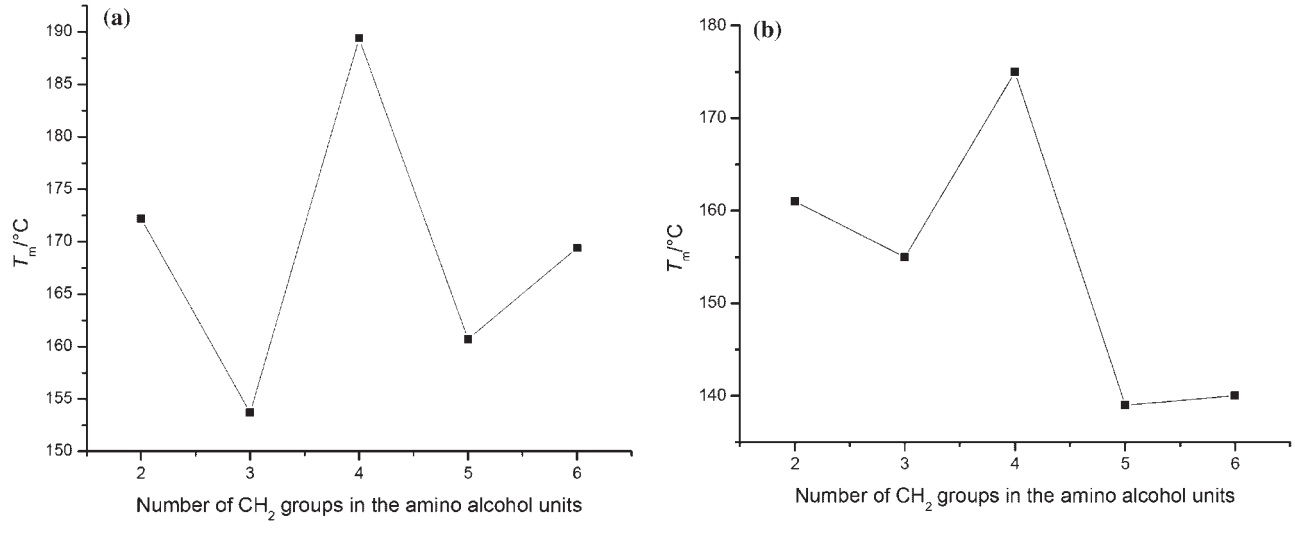



Figure 7. Melting points of polymers (second heating); (a) poly(amide urethane)s **5a-e** obtained via polycondensation of **4a-e** in bulk at 120 °C; (b) poly(amide urethane)s **7a-e** obtained via polycondensation of **6a-e** in bulk at 150 °C.

used as building blocks for the preparation of powder coatings.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